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Note

THERMODYNAMICS OF KCl + WATER + GLUCOSE AND NaCl + WATER + GLUCOSE SYSTEMS FROM VISCOSITY DATA

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At normal temperatures, water has a quasi-crystalline structure [1]. A dynamic equilibrium seems to exist between the three-dimensional hydrogen bonded cluster and the denser monomers: $(H_2O)_c \rightleftharpoons (H_2O)_d$. Electrolytes which dissolve in water have been classified as structure makers or structure breakers, depending on whether the above equilibrium is shifted to the left or right. The inference regarding the structure breaking or structure making effect is derived from viscosity, molar volume or conductance studies. Considerable experimental data and numerous empirical equations are available on the viscosity of dilute aqueous electrolyte and non-electrolyte solutions [2]. However, studies on the viscosity of concentrated aqueous solutions of electrolytes and non-electrolytes are few. In the present communication, the viscosity of KCl and NaCl in aqueous glucose solutions in the concentration range 2.0—0.1 M is reported. Such mixtures constitute ternary systems which will provide indications regarding the types of interactions. The theoretical equation of Einstein [3]

$$\eta_r = 1 + 2.5\phi \tag{1}$$

(where η_r is the relative viscosity and ϕ is the volume fraction) has been modified by Moullik [4], Thomas [5] and Vand [6] to represent the viscosity of aqueous solutions of electrolytes and non-electrolytes at higher concentration. These equations are

Moullik

$$\eta_r^2 = M + K^1C^2 \tag{2}$$

Thomas

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 \tag{3}$$

Vand

$$\eta_r = \frac{2.5\ \phi}{1 - Q\phi} \tag{4}$$

In eqns. (1)—(4), $\phi = C\bar{V}$, where C is the molar concentration and $\bar{V}$ is the molar volume of the solute, Q is an interaction parameter dealing with

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mutual interference between the spheres and with their Brownian motion. A comparative study of these equations over a wide concentration range for a number of salts is reported by Moullik and Mitra [7].

The viscosity B coefficient of the Jones—Dole equation [8]

$$\eta_r = 1 + A\sqrt{C} + BC \tag{5}$$

deals with ion—solvent interactions which take place in a ternary system. Equation (5) is valid for dilute solutions ($C \leqslant 0.1$ M) but not for concentrated solutions ($C \geqslant 0.1$ M). B swamps the effect of A and the equation is reduced to

$$\eta_r = 1 + BC \tag{6}$$

MATERIALS AND METHODS

KCl, NaCl (AnalaR B.D.H.) and glucose (AnalaR B.D.H.) were used as supplied. Calculated amounts of KCl or NaCl and glucose were weighed and the volume made up with conductivity water to prepare the experimental solutions. The density and viscosity measurements were the same as described earlier [1]. The viscosity and density measurements are accurate up to 0.04% and 4×10^6, respectively. The temperatures used were 30, 35, 40 and 45 ± 0.01°C.

RESULTS AND DISCUSSION

The B coefficients were obtained using eqn. (6) in the concentration range studied (2.0—0.1 M), and are given in Table 1 together with the B values of sucrose [9] and urea [10]. The different parameters of Moullik and the rearranged forms of Thomas [eqn. (7)] and Vand [eqn. (8)] are obtained by employing both graphical and least squares methods and are recorded in Table 2.

$$\frac{\eta_r - 1}{C} = 2.5\bar{V} + (K_s\bar{V}^2)\,C \tag{7}$$

$$\frac{1}{C} = 1.085\bar{V}\frac{1}{\log \eta_r} + K_s\bar{V} \tag{8}$$

In eqns. (7) and (8) K_s and K are used in place of 10.05 in Thomas's equation and Q in Vand's equation, respectively. It is possible to calculate these parameters since the viscosity data fit well with eqns. (4), (7) and (8).

According to Stokes and Mills [11], the viscosity B coefficient is due to three contributions: η^E, the positive increase due to slope and size of an ion; η^A, the increase due to the alignment or orientation of the polar molecules by the ionic field; and η^D, the decrease in the viscosity arising due to the distortion of the solvent structure by the ions. Therefore the B coefficients can be discussed in terms of the viscosity effects. Inspection of Table 1 shows that the B values of the salts decrease with increasing percentage of sucrose,

TABLE 1

B coefficients (l mole^{-1})

Wt. % of non-electrolyte	KCl				NaCl			
	30	35	40	45	30	35	40	45
Glucose + water								
5	0.2125	0.2078	0.2054	0.1905	0.3252	0.3195	0.3200	0.2940
10	0.1865	0.1800	0.1760	0.1650	0.2953	0.3030	0.3130	0.3242
15	0.1750	0.1730	0.1640	0.1680	0.2900	0.2806	0.2897	0.2965
20	0.1650	0.1700	0.1554	0.1650	0.2740	0.2896	0.2900	0.3030
Sucrose + water								
5	0.1750	0.1842	0.2000	0.2030	0.2600	0.2700	0.2800	0.2835
10	0.1572	0.1786	0.1666	0.1750	0.2400	0.2697	0.2596	0.2647
15	0.1430	0.1500	0.1500	0.667	0.2304	0.2500	0.2500	0.2569
20	0.1375	0.1184	0.1324	0.1500	0.2200	0.2245	0.2347	0.2396
Urea + water								
5	0.925	0.1904			0.2950	0.2900		
10	0.1760	0.1666			0.2850	0.2900		
15	0.1650	0.1640			0.2800	0.2750		
20	0.1550	0.1523			0.2650	0.2750		

TABLE 2

The parameters obtained using the equation of Moullik and the slightly modified equations of Thomas and Vand

Glucose (wt. %)	KCl							
	30°C		35°C		40°C		45°C	
	Moullik's eqn.							
	M	*K'*	*M*	*K'*	*M*	*K'*	*M*	*K'*
5	1.02	0.38	1.02	0.44	1.01	0.44	1.01	0.51
10	1.03	0.39	1.02	0.45	1.01	0.52	1.01	0.52
15	1.01	0.42	1.01	0.46	1.02	0.62	1.02	0.53
20	1.000	0.44	1.01	0.48	1.00	0.64	1.03	0.55
	Thomas's eqn.							
	$\overline{V}$	*K*	$\overline{V}$	*K*	$\overline{V}$	*K*	$\overline{V}$	*K*
5	0.052	1.11	0.053	0.97	0.052	0.62	0.051	0.23
10	0.050	1.22	0.049	0.92	0.048	0.67	0.046	0.25
15	0.049	0.88	0.047	0.93	0.047	0.23	0.044	0.27
20	0.043	0.89	0.043	0.77	0.43	0.34	0.039	0.28
	Vand's eqn.							
	$\overline{V}$	K_s	$\overline{V}$	K_s	$\overline{V}$	K_s	$\overline{V}$	K_s
5	0.054	−2.4	0.051	−1.11	0.048	−0.98	0.047	−3.4
10	0.048	−3.2	0.047	−1.25	0.044	−0.99	0.042	−3.2
15	0.047	−3.1	0.043	−1.36	0.043	−0.94	0.040	−4.8
20	0.040	−1.1	0.041	−1.37	0.040	−0.95	0.037	−5.2

glucose and urea. This indicates that the viscosity decreases because of distortion of the solvent structure, i.e. η^D increases. The decrease in *B* value is found to be of the order: sucrose + water > urea + water > glucose + water, which is also the order of ion—solvent interaction.

This can be explained as follows. Sucrose contains more hydroxy groups than *d*-glucose and those hydroxy groups participate with the formation of a hydrogen bond with water molecules and hence the water structure breaks and so sucrose is more of a structure breaker than glucose. As regards urea, it can be said that urea is alkaline and water both acts as a proton donor and acceptor; hence in the mixture of urea and water, the structure is likely to be broken. Secondly, urea, due to keto-enol tautomerism in solution, may contain one hydroxy group which participates in the formation of a hydrogen bond with water molecules and structure breaking as observed.

The *B* coefficient of KCl is found to be less than that of NaCl. Ions with greater crystal radii and small charge density, K^+, would have a weak orienting effect in the first layer. Therefore, η^E and η^A will be small.

There also exists a considerable amount of distortion in the vicinity of such ions due to the competition between the ionic field and bulk structure, and consequently η^D will be large. Thus *B* will be smaller for K^+ salts than for Na^+ salts (Table 1), so the order of ion—solvent interaction is $K^+ > Na^+$.

The equations of Thomas and Vand in slightly modified forms and Moul-

NaCl							
30°C		35°C		40°C		45°C	
M	K'	M	K'	M	K'	M	K'
1.00	0.52	1.00	0.54	1.00	0.71	1.02	0.75
1.00	0.53	1.00	0.54	1.00	0.72	1.01	0.76
1.00	0.54	1.00	0.63	1.02	0.73	1.01	0.77
1.00	0.56	1.00	0.67	1.01	0.74	1.00	0.77
$\bar{V}$	K	$\bar{V}$	K	$\bar{V}$	K	$\bar{V}$	K
0.088	1.02	0.882	0.64	0.085	0.62	0.079	0.51
0.077	0.98	0.075	0.63	0.073	0.70	0.073	0.50
0.075	0.86	0.070	0.62	0.071	0.54	0.070	0.42
0.072	0.62	0.070	0.60	0.069	0.50	0.067	0.38
$\bar{V}$	K_s	$\bar{V}$	K_s	$\bar{V}$	K_s	$\bar{V}$	K_s
0.084	−5.1	0.084	−5.7	0.084	−6.1	0.072	−7.2
0.073	−5.2	0.071	−5.8	0.069	−6.2	0.066	−7.3
0.071	−5.4	0.069	−5.9	0.068	−6.3	0.062	−7.3
0.070	−5.6	0.072	−5.9	0.067	−6.4	0.060	−7.4

lik's equation in its original form hold good for solutions of KCl and NaCl reported here. It is evident from the results given in Table 2 that the viscosity data of a ternary system cannot be explained by a single equation. The values of $\bar{V}$ for KCl and NaCl obtained from the equations of Thomas and Vand are in good agreement and these values decrease with increase in non-electrolyte concentration. This may be ascribed to the decrease in the electrostatic attraction between the water dipole and the ion, as a large number of water molecules are not available in the cosphere of the ions.

Interpretation of the viscous flow for electrolytic solutions in water according to the theory of absolute reaction rates has been done by Nightingale and Benck [12], who have calculated the energy of activation, ΔE (which does not differ appreciably from activation enthalpy), free energy of activation, ΔG, and entropy of activation, ΔS, for water and a number of electrolytic solutions. Proceeding along similar lines, ΔG, ΔE and ΔS for KCl and NaCl in 5, 10, 15 and 20% of glucose have been calculated at 35° C and the results, along with those of sucrose solutions, are recorded in Table 3. It is observed that the energy and entropy of activation for viscous flow are greater than those of the solvent, but the free energy of activation is almost unchanged though it increases slightly with increase in non-electrolyte content. The abnormally large energies and entropies of activation are attributed

TABLE 3

Activation parameters

Non-electrolyte (wt. %)		Glucose + water			Sucrose + water		
		ΔG (kJ mole^{-1})	ΔE (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})	ΔG (kJ mole^{-1})	ΔE (kJ mole^{-1})	ΔS J K^{-1} mole^{-1})
5	Solvent	10.143	7.655	−8.08	9.149	6.456	−9.08
	KCl	10.433	13.978	11.51	9.851	12.851	12.81
	NaCl	10.551	10.143	10.31	10.215	11.862	10.32
10	Solvent	10.492	7.256	−10.50	9.545	6.575	−9.81
	KCl	10.753	15.010	14.86	10.010	14.545	13.81
	NaCl	10.981	11.456	11.35	10.353	12.243	12.21
15	Solvent	11.173	5.805	−17.43	9.992	6.854	−10.23
	KCl	11.365	15.240	12.58	10.748	13.541	12.78
	NaCl	11.474	12.581	13.55	11.010	9.423	11.54
20	Solvent	11.740	5.080	−21.62	10.231	7.354	−12.43
	KCl	11.893	16.020	13.40	10.892	16.020	12.40
	NaCl	12.110	12.471	12.85	11.155	12.421	11.38

to the excess energy necessary to break the hydrogen bonding in the solution.

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